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Large phase fluctuations near T_1 and phase pinning in incommensurate $\text{ThBr}_4 : \text{Gd}^{3+}$ through E.S.R. measurements

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Résumé. — Récemment la coexistence de raies « comme normales » et incommensurables dans les spectres R.M.N. de ^{87}Rb , a été observée au-dessous de T_1 dans Rb_2ZnBr_4 , et a été interprétée en termes d'ondes stationnaires de fluctuations de phase entre des défauts épingleurs. Nous analysons un effet identique dans les spectres R.P.E. de $\text{ThBr}_4 : \text{Gd}^{3+}$. Nous excluons un effet extrinsèque de la sonde E.P.R. qui ne manifeste aucune tendance à accrocher la phase et nous montrons que des fluctuations de phase inhomogènes peuvent rendre compte des observations. Une application sommaire du modèle développé par Blinc indique que le « pinning » apparaît probablement sur les dislocations.

Abstract. — Recently, the coexistence of « normal-like » and incommensurate ^{87}Rb N.M.R. lines have been observed in Rb_2ZnBr_4 below T_1 , and has been interpreted in terms of a standing wave regime of phase fluctuations between pinning defects. We analyse a similar effect in the E.P.R. spectra of $\text{ThBr}_4 : \text{Gd}^{3+}$. We rule out the possibility of an extrinsic pinning effect due to the E.P.R. probe and we show that inhomogeneous phase fluctuations can account for the observation. A crude application of the model developed by Blinc indicates that the average distance between pinning centres is compatible with their being dislocations.

Introduction.

ThBr_4 (β) undergoes a normal to incommensurate structural phase transition at 95 K [1-6]. Neutron scattering data [3] give a precise description of the soft coordinates and of the associated displacement field below T_1 . No lock-in transition is observed down to 10 K, and the modulation obeys a plane wave regime. An important and rare result [3] is the unambiguous observation of the phason and amplitudon modes below T_1 , in accordance with theory.

Two types of local measurements with the help of extrinsic probes have been realized. The luminescence spectrum of U^{4+} [6] at 4 K would seem to indicate a partial phase pinning by the U^{4+} impurities. In a previous work we have shown the sensitivity of the E.P.R. Gd^{3+} -n.n.n Br^- vacancy to the transition [5].

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In this Letter we focus our interest on :

i) the evolution of the E.P.R. lineshape across the incommensurate phase in order to investigate the possibility of phase pinning by the probe.

ii) a particular effect limited to the temperature range $T_1 - 2.7 < T < T_1$ which we interpret in terms of large phase fluctuations. A similar effect has been recently observed by ^{87}Rb N.M.R. spectroscopy [7] in Rb_2ZnBr_4 .

1. Theoretical background.

The static displacement field below 95 K can be represented by a superposition of a rotation and of a twist of the Br^- tetrahedra [3] : surrounding the Th^{4+} ions

$$\mathbf{u}(z) = \mathbf{r}A \cos(kz + \phi_0) + \mathbf{t}\alpha A \sin(kz + \phi_0)$$

\mathbf{r} and \mathbf{t} represent normalized vectors for the rotation and for the twist, A is the amplitude and $\phi = kz + \phi_0$ is the phase of the plane wave modulation, z is the coordinate of the Br^- along the incommensurate wave vector $\mathbf{k}(0, 0, k)$, α is a mixing coefficient between the two components, the phases of which differ by $\frac{\pi}{2}$ [3].

The static displacement field induces a local shift of the E.P.R. lines of a paramagnetic probe substituted for Th^{4+} . A power expansion limited to second order gives :

$$\Delta H(\phi) = A \{ h_1(r) \cos \phi + h'_1(t) \sin \phi \} + A^2 \{ h_2(r) \cos^2 \phi + h'_2(t) \sin^2 \phi + h''_2 \sin \phi \cos \phi \}.$$

We have assumed a short range probe. In the critical region one has $A \propto (T_1 - T)^\beta$. The parameters h_i depend on the E.P.R. transition and on the orientation of the magnetic field ; they are not dependent on temperature. Within the model [8] the static line shape is given by :

$$I(H) = \int_0^{2\pi} f(H - \Delta H(\phi)) d\phi$$

and exhibits a continuous absorption background with singularities centred at resonance fields such as $\frac{d\Delta H(\phi)}{d\phi} = 0$. $f(H - \Delta H)$ represents a local line shape with a finite line width including various kinds of broadening irrelevant to the transition.

The static line shape can be modified if the local extrinsic probe behaves as a phase pinning defect. Then some value of the phase is locally favoured, and one should obtain a spurious singularity at the corresponding values of ΔH . Such a singularity does not mirror the modulation of the bulk.

Moreover a simple theory of structurally incommensurate phase predicts that the modulation wave can move freely [7, 9]. Generally, discrete lattice effects or intrinsic defects lock the modulation to the underlying lattice [7]. Just below T_1 , the thermal energy should be able to overcome the pinning energy and restore a floating incommensurate phase [7], inducing spatial and temporal fluctuations of the phase ϕ . In other words since the phason mode has in principle no gap, one may expect substantial thermal fluctuations of the local phase ϕ :

$$\phi = kz + \phi_0(z, t).$$

Let us consider a local E.P.R. line shift given by

$$\Delta H = h_1 A \cos(kz + \phi_0(z, t)).$$

This line shift permits us to define a characteristic frequency :

$$\nu_c = \left(\frac{2 g \beta h_1}{h} \right) A$$

and we may consider two limiting cases :

— The phase fluctuations are slow with respect to ν_c and the E.P.R. measurement gives an instantaneous response. The random phase fluctuations do not modify the E.P.R. spectrum and one observes two edge singularities separated by

$$\Delta H = 2 h_1 A.$$

— The phase fluctuations are fast and motional narrowing occurs. A simple calculation, gives :

$$\Delta H(z) = \exp\left(-\frac{\langle \phi_0^2 \rangle}{4}\right) h_1 A \cos(kz).$$

We have assumed homogeneous Gaussian fluctuations with mean square $\langle \phi_0^2 \rangle$. It turns out that the phase fluctuations of mean square amplitude of order $\frac{\pi}{2}$ induce an important spectral narrowing of the edge singularities and can lead to an unresolved, « normal-like », single line. This effect is quite similar to the enhancement of the Debye-Waller factor of satellites reflections by phase fluctuations, in scattering experiments [10].

2. E.P.R. line shape below T_1 .

In ThBr_4 : Gd^{3+} , one observes several paramagnetic centres : Gd^{3+} substituted for Th^{4+} at D_{2d} sites, Gd^{3+} associated to nearest neighbour (n.n) Br^- vacancy, Gd^{3+} associated to next nearest neighbour (n.n.n) Br^- vacancy. This last point defect is the most easily tractable to study the phase transition [5] by E.P.R. We shall consider the associated high field E.P.R. line corresponding to $M_s = \frac{5}{2} \leftrightarrow \frac{7}{2}$, for H in the (001) plane at about 25° away from [100], [5].

The concentration of Gd^{3+} is about 100 p.p.m., and the doping induces the same concentration of extrinsic Br^- vacancies. It is worth noting that the mean distance between paramagnetic probes is of the order of ~ 20 in lattice parameter units.

Typical line shapes are represented in figures 1, 2 and 3. Between $T_1 - 2.8$ K and $T_1 - 15$ K, one observes two edge singularities (Fig. 1), i.e. a typical incommensurate line shape. This type of spectra have been previously analysed [5]. The splitting between the singularities mainly arises from the rotational component of the displacement field and exhibits a critical behaviour $\Delta H \propto A \propto (T_1 - T)^\beta$ with $\beta = 0.34 \pm 0.02$. At lower temperature, three and four singularities become apparent. Their origin is doubtful since phase pinning by the probe may alter the line shape. To clarify this point, we have used the theoretical model of section 1 to reconstruct the experimental lines. The computation results indicate that the modification of the experimental lines shape are satisfactorily explained by an increasing contribution of second order terms associated with an increase of the amplitude of the modulation when the temperature decreases. An excellent agreement, between the theoretical model and the experimental results is obtained in the temperature range T_1 , $T_1 - 15$ K, with $A \propto (T - T_1)^{0.35}$ [3] and all h_i 's constant (Fig. 1). Below, a good agreement is obtained (Fig. 2) with the same values of the h_i 's. Nevertheless, inhomogeneous saturation effects, consistent with relaxation mechanisms induced by the phason mode, alter the line shape which has to be more carefully analysed, at low temperature, saturation

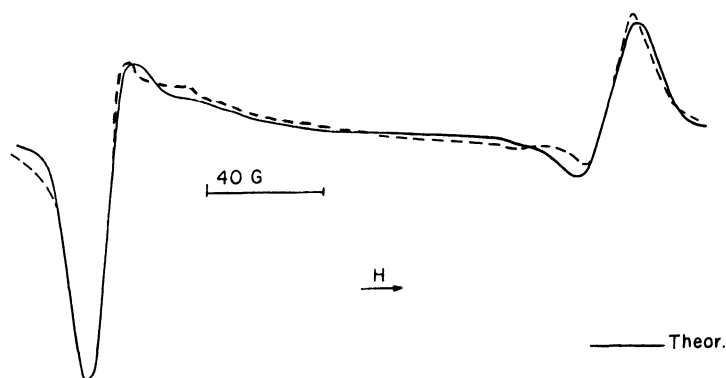


Fig. 1. — Experimental spectrum at $T_1 = 7$ K (dashed line) compared to the theoretical prediction (full line).

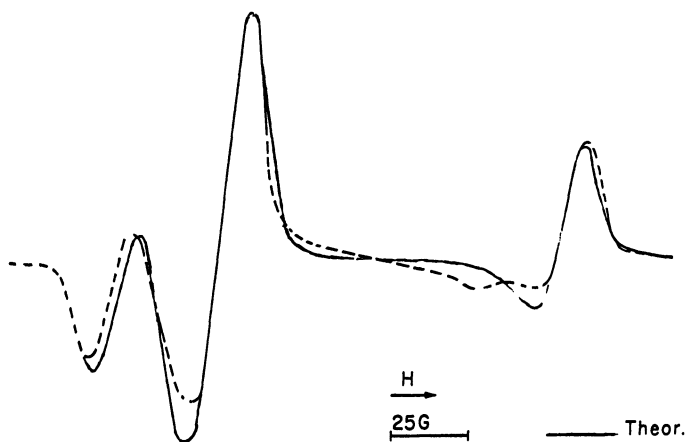


Fig. 2. — Experimental spectrum at $T_1 = 15$ K (dashed line), and theoretical spectrum (full line). One notices the third singularity attributed to a $\cos^2 \phi$ terms which become important at lower temperatures.

effects becoming important. It is worth noting that the best fit of the theoretical line shape to the experimental one is obtained by considering Gaussian local line shape $f(H - \Delta H)$.

We conclude that the line shape mirrors the plane wave modulation regime, the two component displacement field and their phase difference of $\frac{\pi}{2}$. Moreover the probe, which is a point defect, with charge misfit and compensation by a near vacancy, does not exhibit any tendency towards phase pinning. For comparison, the U^{4+} impurity, which fits the host [6], would seem to induce some degree of phase pinning. We suggest similar investigations on various point defects to clear the mechanisms of phase pinning which is generally invoked and still rather obscure.

3. Evidence for large phase fluctuations near T_1 .

The experimental lines above $T_1 = 2.7$ K are represented in figure 4. In this temperature range, one observes the coexistence of an incommensurate spectra and of a « normal like » line which disappears below $T_1 = 2.7$ (Figs. 4, 1). This cannot arise from a critical temperature gradient

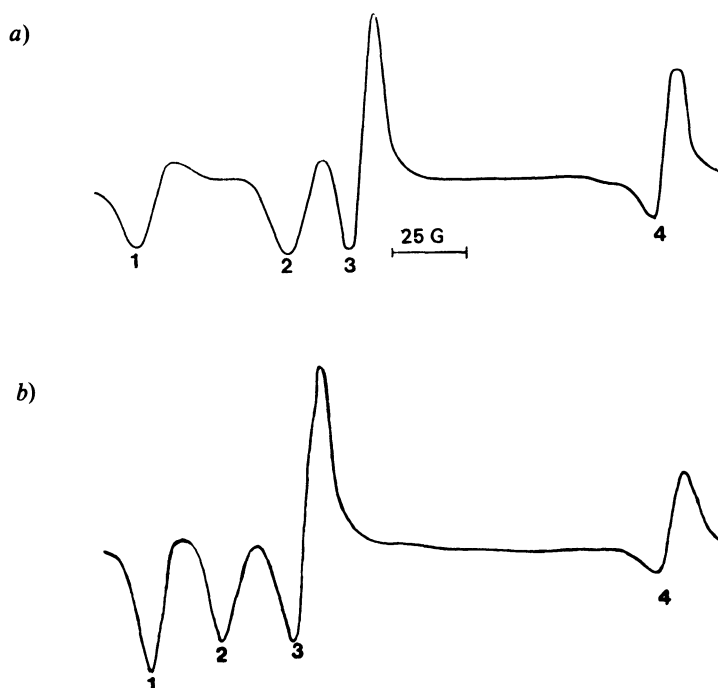


Fig. 3. — a) Experimental spectrum at $T_1 = 35$ K. b) The theoretical one (not fitted), which permits us to establish the validity of the model. The singularity 2 arises from twist terms.

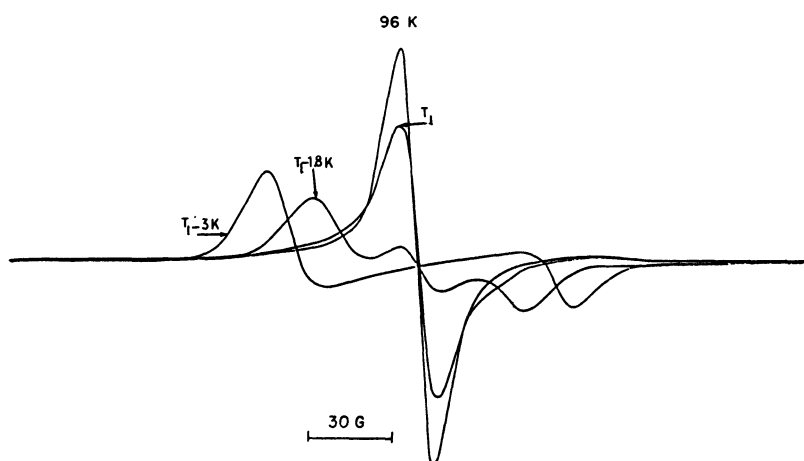


Fig. 4. — Experimental spectra near T_1 . One notices at $T_1 - 1.8$ K a coexistence of « incommensurate » singularities with a « normal like » line.

in the bulk which would smooth the edge-singularities of the « incommensurate » line. This effect delays the appearance of the characteristic edge singularity spectra at T_1 and prevents a direct determination of the critical temperature.

We have studied the « normal » line above T_1 and the « normal like » line below T_1 , by assuming a line shape given by

$$I(H) = N \int \exp \left[- \left(\frac{H - H_1}{h_G} \right)^2 \frac{1}{1 + \left(\frac{H_1 - H_0}{h_L} \right)^2} dH_1 \right]$$

where N is a normalization constant and H_0 is the central resonance field.

This model has been set up to include static contributions through the Gaussian parameter h_G and dynamical contributions through the Lorentzian parameter h_L to the line width and the line shape. At 110 K the parameters are $h_G = 3.64$ G and $h_L = 5.11$ G, and can be attributed to inhomogeneous broadening by superhyperfine interactions and to homogeneous broadening by non critical fluctuations, respectively.

The parameters have been fitted to the experimental line shapes. The results are represented in figure 5 where we have plotted the Gaussian δh_G and the Lorentzian δh_L critical broadening of the E.P.R. line. One can identify T_1 by a change of the Gaussian broadening δh_G (Fig. 5). This determination of T_1 agrees with the temperature determined from the critical behaviour of the edge-singularity spectrum (Fig. 6).

Above T_1 , the line shape and the line width have a normal critical behaviour, frequently observed near structural transitions. Increasing fluctuations and critical slowing down, associated with a soft mode plus a central peak account for it. At $T_1 - 7$ K the local line shapes involved in the normal « incommensurate » spectrum (Fig. 1) are Gaussian and narrow. This indicates a weak influence of fluctuations. The « normal like » line below T_1 and the normal line above T_1 , exhibit a continuous behaviour of their Lorentzian broadening, figure 6. This is an indication that the « normal like » line may arise from motional narrowing of an « incommensurate »

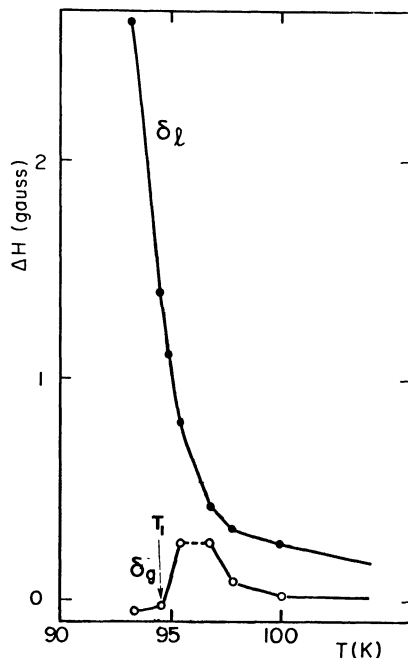


Fig. 5. — Critical Gaussian δh_G and Lorentzian δh_L broadening of the single line above and below T_1 .

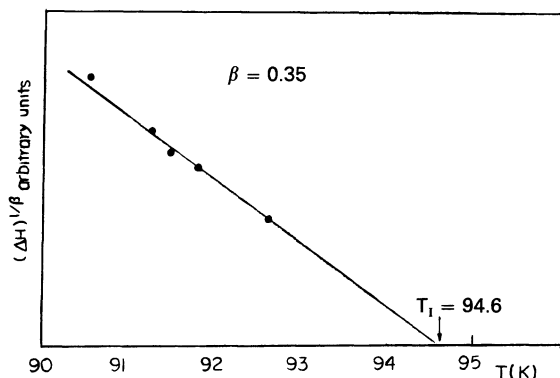


Fig. 6. — Graphical determination of T_1 by extrapolation of the edge singularity spectrum.

spectrum by large fluctuations as indicated by the model developed in section 1. Indeed this model applies to the temperature range $[T_1, T_1 - 2.7]$ in which the preponderant term of the line shift is $A \cos \phi$. Nevertheless one cannot explain the coexistence of edge singularities and of the central line by homogeneous phase fluctuations. One has to assume that the phase is static in some regions of the crystal $\langle \phi_0^2 \rangle \simeq 0$ and exhibits large fluctuations in other ones $\sqrt{\langle \phi_0^2 \rangle} \sim \frac{\pi}{2}$. N.M.R. spectra of ^{87}Rb have given evidence for the same type of phenomenon [7] in Rb_2ZnBr_4 .

4. Standing-wave model.

According to the model developed by Blinc [7], pinning defects are involved in the interpretation of the observed spectra. Between these defects, distant by l , the phason mode would lead to standing waves, creating regions of small and large fluctuations at the nodes and antinodes. For large l , low frequencies and therefore large thermal fluctuations are allowed. In a crude description one may write : $l \simeq \frac{C_p}{2\nu} = \frac{\lambda}{2}$ for the lowest allowed frequency. For a certain cut off length l_c , the amplitude of fluctuation is too small for substantial motional narrowing. One may state the condition $l = \frac{C_p}{2\nu} > l_c$ or $\nu < \frac{C_p}{2l_c}$ with C_p the phason velocity.

On the other hand the frequency has to be large enough with respect to the characteristic E.P.R. frequency ν_c :

$$\nu > \nu_c = \frac{2g\beta h_1 A}{h}.$$

At $T_1 - 2.7$ K, the « normal like » line disappears. This means that the distance between pinning defects is too small to fulfil the motional narrowing conditions. With $C_p = 2 \times 10^{12}$ (in units of lattice parameter s^{-1}) [3], one finds $l = l_c = 8 \times 10^3$ (in units of lattice parameter).

This distance more likely corresponds to dislocations than to point defects. The known point defects induced by the Gd^{3+} doping are much less distant, which implies that the paramagnetic probe does not pin the phase.

Conclusion.

We have shown that the E.P.R. probe used to investigate the incommensurate phase, does not pin the phase of modulation and reflects correctly the plane wave displacement field. The probe is not responsible for the coexistence of « incommensurate » and « normal like » lines. This interesting effect can be analysed in terms of inhomogeneous phase fluctuations due to phase pinning defects. A very simple application of the standing wave model, previously developed by Blinc, indicates an average distance between pinning defects compatible with their being dislocations.

Nevertheless a definite interpretation of this effect, also observed in Rb_2ZnBr_4 , needs more experimental and theoretical investigations.

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